Original Article

Application of Ion Mobility-Mass Spectrometry to the Study of Ionic Clusters: Investigation of Cluster Ions with Stable Sizes and Compositions

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Stable cluster sizes and compositions have been investigated for cations and anions of ionic bond clusters such as alkali halides and transition metal oxides by ion mobility-mass spectrometry (IM-MS). Usually structural information of ions can be obtained from collision cross sections determined in IM-MS. In addition, we have found that stable ion sizes or compositions were predominantly produced in a total ion mass spectrum, which was constructed from the IM-MS measurement. These stable species were produced as a result of collision induced dissociations of the ions in a drift cell. We have confirmed this result in the sodium fluoride cluster ions, in which cuboid magic number cluster ions were predominantly observed. Next the stable compositions, which were obtained for the oxide systems of the first row transition metals, Ti, Fe, and Co, are characteristic for each of the metal oxide cluster ions.

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INTRODUCTION

Ion mobility spectrometry, IMS, has become one of the important techniques in ion analysis of gas-phase complex species such as macromolecules, atomic and molecular clusters, and nanoparticles.^{1,2)} This technique originally developed in the field of atomic and molecular physics more than 50 years ago, in order to unveil the interactions between a neutral particle and an ion.³⁾ IMS has also been developed in the field of analytical chemistry as a simple gas-phase ion analysis method which is not necessary to use high vacuum apparatus like mass spectrometry, and now it is applied to chemical analysis of toxic or explosive compounds in airports or in battlefields.⁴⁾

In the drift tube method of the original IMS, a pulse of ion swarm is injected into a gas cell (ion drift tube, ion drift cell) in which an electrostatic field, E , is applied and buffer gas is admitted. The injected ions reach a constant drift velocity, v_d , which is determined by the balance of acceleration with the electric field and the deceleration by collisions with the buffer gas atoms. The v_d value is proportional to E , that is,

$$v_d = KE, \quad (1)$$

in which the coefficient K is defined to be an ion mobility.⁵⁾ The mobility K is dependent on the buffer gas pressure and

the cell temperature. However, reduced ion mobility, K_0 , which is reduced at the standard conditions (760 Torr and 273.15 K), is a physical quantity intrinsic to the ion and the buffer gas. The ion mobility has also been formulated by gas kinetic theory as,

$$K = \frac{3e}{16N} \left(\frac{2\pi}{k_B \mu T_{\text{eff}}} \right)^{1/2} \frac{1}{\Omega^{(1,1)}} \quad (2)$$

where e is the elementary charge, N is the number density of the buffer gas, k_B is the Boltzmann constant, μ is the reduced mass of the ion and the buffer gas atom, and $\Omega^{(1,1)}$ is a collision integral representing an average over collision energy, orientations and inelastic collisions.⁵⁾ When we treat the ion and the neutral as hard spheres without internal states, $\Omega^{(1,1)}$ reduces to the hard-sphere collision cross section, Ω . Therefore the cross section Ω can be determined from Eq. (2), in which the mobility value determined in the IMS experiment is used for K . Moreover, the structure of the complex ion can be determined by comparing the Ω value thus determined from the experiment with the theoretically determined, orientation-averaged cross section. This type of structural research was fulfilled using a technique of ion mobility-mass spectrometry, IM-MS, which is the combination of IMS with mass spectrometry. Ion structures of several atomic and molecular clusters, such as semiconductor clusters,⁶⁻⁹⁾ metal clusters,¹⁰⁻¹⁴⁾ ionic bond clusters^{15,16)} and so on, were already investigated by IM-MS.

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From a couple of years ago the authors' group started IM-MS experiment on the metal oxide clusters and determined the oxide cluster ion structures for the transition metal atoms, Zn,¹⁷⁾ Co¹⁸⁾ and Fe.¹⁹⁾ Among those studies, we were necessary to obtain cluster ion mass spectra, which were difficult to obtain at a one-time measurement because of the ion packet dispersion due to the wide range of ion mobilities. From a "total ion" mass spectrum which we constructed in the IMS measurement, we have found that it reveals the stable ion mass distribution in which the initially produced ions were dissociated to other ions with stable cluster sizes or stable chemical compositions as a result of collisions with buffer gas atoms in the drift cell. The size or composition distribution resulting from collision-induced-dissociation (CID) reactions are sensitively dependent on the ion injection energy into the cell.

In this paper we present the results of mass spectrometric study from the IMS measurement of ionic bond cluster ions. Firstly from the results of sodium fluoride cluster ions, we have confirmed that the stable clusters (magic number clusters) were predominantly formed by CID reactions in the cell.²⁰⁾ Next we show the results of investigation of stable chemical compositions for first-row transition metal oxide cluster ions. As for the stable composition of the transition metal oxides, there have been several investigations using CID,^{21,22)} photodissociation²³⁾ and thermal heating.²⁴⁾ However no definite was known from such experiments so far. Finally we have discussed the nature of composition dependence on the sort of metal atoms, and also on the polarity of the ions (between positive and negative ions).

EXPERIMENTAL

The experiments were performed using a home-made, differentially-pumped apparatus composed of a cluster-ion source, an ion drift cell for ion mobility spectrometry, and a reflectron type time-of-flight (TOF) mass spectrometer, as shown in Fig. 1.^{18–20,25)} Either of the positive or negative ions were examined by this apparatus, by changing the polarity of voltages applied in the electrodes. Cluster ions were produced by combination of a laser vaporization method with subsequent chemical reactions. For example, metal oxide cluster ions were produced by laser ablation of a metal rod in an aluminum block with a second harmonic of a pulsed Nd:YAG laser (New Wave, Polaris), and by subsequent reaction with oxygen which were expanded from a pulsed valve (General Valve, Series 9) with He gas. The detailed

experimental conditions were optimized by monitoring the produced cluster ion signals. For example, the stagnation pressure and the O₂ concentration in He were 4 atm and 5% for production of titanium oxide cluster ions and 3 atm and 2.5% for iron oxide cluster ions. On the other hand, sodium fluoride cluster ions were produced by laser vaporization of a Na rod and subsequent reaction with fluorine-containing molecules such as C₆F₆ or SF₆. Cluster ions thus produced were then injected into the ion drift cell by a pulsed electric field, which is hereafter denoted as an "ion gate" pulse. The strength of the ion-gate electric field determined the injection energy of the ions, E_i , which was typically controlled between 50–350 eV. The ion drift cell was 10 cm long, and its entrance and exit holes were 2.5 mm in diameters. The drift electric field was typically 10.0 V/cm. Helium gas was introduced into the cell as buffer gas typically up to 1.0 Torr. The temperature of the ion drift cell was able to be lowered down to about 170 K by introducing liquid nitrogen into a copper tube surrounding the cell.

The ions, which were separated by their cross sections in the ion drift cell, exited from the cell and finally reached a Wiley–McLaren type acceleration region of the TOF mass spectrometer. Here, the ions originally injected into the drift cell at a given time, $t=t_0$, were accelerated by a pulsed electric field at a given time, $t=t_0+\Delta t$, where Δt is a time delay from the timing of the ion gate pulse. We hereafter call this delay time "arrival time," because the delay corresponds to the time arriving at the acceleration region of the TOF mass spectrometer for a given ion isomer after entering the drift cell. The ions, which were accelerated with an energy of 1.8 keV by the pulsed electric field, were then mass separated in the reflectron TOF mass spectrometer, and their mass spectrum with the given Δt were measured.

The present measurement of ion mobility-mass spectrometry was composed of two steps; one was the separation by collision cross sections and the other was the separation of their mass. The cluster ions entering the ion drift cell were accelerated by the drift electric field, while they were decelerated by the collisions with He buffer gas atoms. Finally the ions reached a certain speed, which depends on the collision cross sections of cluster ions with He. Ions having compact structures passed through the drift cell faster than those with larger cross sections. Typically the number of collisions between cluster ions with He atoms were estimated to be 4000 for Na₇F₆⁺ and 6000 for Na₁₃F₁₂⁺ in the present experimental condition. The ions were then mass-separated in the reflectron TOF mass spectrometer after accelerating at their corresponding arrival times. We thus obtained a series of TOF mass spectra sequentially by tuning the arrival time. The obtained mass spectra were represented as a two-dimensional contour plot of TOF vs. arrival time. We also obtained a plot of arrival time distribution, ATD, in which the total ion intensity of a certain TOF peak was also plotted as a function of arrival time. The peak of the ATD plot corresponds to a representative arrival time of a certain isomer with the selected mass.

As mentioned above, the ions exited the ion drift cell have diffuse spatial distribution depending on their mobilities. Therefore it is necessary to sum up all the mass spectra configuring the 2D contour plot, in order to obtain total mass spectrum. The total ion mass spectrum thus obtained has a prominent injection energy E_i dependence into the drift

Fig. 1. Schematic view of the experimental apparatus.

cell, although E_i was usually kept low in the typical IM-MS experiments in order to obtain reliable ion mobility values. In this paper we can discuss the stable size or composition of the clusters from the E_i dependence, as mentioned in the following sections.

RESULTS AND DISCUSSION

Sodium fluoride cluster cations and anions—Confirmation of stable ion formation in the ion-mobility experiments

For the past more than 30 years, alkali halide clusters and their ions were investigated both experimentally and theoretically.^{26–31)} This type of clusters are composed of alkali cations (M^+) and halogen anions (X^-), and therefore the stable cluster cations have a composition with one more alkali atoms than halogen atoms, $M_nX_{n-1}^+$, and *vice versa* for the stable cluster anions, $M_{n-1}X_n^-$. Main feature on the geometrical structures obtained from the past experimental and theoretical studies was that the stable structures correspond to cuboid subunits of bulk crystals. This is the reason why alkali halide clusters are often called as nanocrystals.²⁶⁾ For example, as for the sodium fluoride cluster cations, $Na_nF_{n-1}^+$, stable cluster sizes known as magic numbers in mass spectra are $n=5, 14, 23, 32, 38, 53, 63$, and so on, all of which correspond to the face centered cubic rectangles, as shown in Fig.

Fig. 2. Examples of cuboid structures of magic number clusters of $Na_nF_{n-1}^+$ cluster ions. Number of atoms on each side of the cuboids are shown in parentheses.

2. These magic numbers were observed in mass spectra of several types of experiments, in which the cluster ions were dissociated into stable ions by collisions with other gases or with solid surfaces.^{26,32)}

As noted in the experimental section, the two-dimensional contour plot of TOF vs. arrival time was obtained in the present IM-MS experiment. Figure 3 shows the contour plot obtained for sodium fluoride cluster cations $Na_nF_{n-1}^+$, with n up to *ca.* 90. The arrival time is inversely proportional to the drift velocity v_d and the ion mobility K in Eq. (1), and thus it is proportional to the collision cross section Ω . Therefore we have easily found from the plot that the cross section in general increases with the cluster size, although the increment is not smooth with the size. More precisely, we have determined the cross section of each cluster ion from Eq. (2), and compared with the orientation-averaged cross sections obtained by theoretical calculations. From these analyses, geometrical structure was determined for each cluster ion.²⁰⁾ In particular, the cross sections of above magic number clusters were explained by the cuboid structures.

Figure 4 shows total ion mass spectrum of sodium fluo-

Fig. 3. Two dimensional contour plot of time-of-flight vs. arrival time of $Na_nF_{n-1}^+$ cluster ions, $n=2$ to *ca.* 90. The ion injection energy $E_i=137.5$ eV.

Fig. 4. Total ion time-of-flight mass spectra of sodium fluoride cluster ions obtained in the present experiment. (a) Positive ions, (b) negative ions.

ride cluster cations $\text{Na}_n\text{F}_{n-1}^+$ obtained by summing up each mass spectrum at a given arrival time constituting the 2D plot of Fig. 3, as mentioned in the experimental section, along with that of cluster anions $\text{Na}_{n-1}\text{F}_n^-$ obtained in the same manner. In both of these mass spectra we have found magic numbers of $n=5$ ($3\times3\times1$), 14 ($3\times3\times3$), 23 ($3\times3\times5$), 38 ($3\times5\times5$), 63 ($5\times5\times5$), and 88 ($5\times5\times7$), all of which have structures of cubic nanocrystals noted above. Both cation and anion mass spectra have similar size distributions except for the background at high mass region in the cation mass spectrum. This background was due to low signal-to-noise ratio in the 2D plot (Fig. 3). The observed magic numbers are more obvious and wider size range than those observed in previous mass spectrometric studies.²⁶⁾ This observation is rationalized as follows: Sodium fluoride cluster ions generated in the cluster source were injected into the ion drift cell by a pulsed electric field with injection energies E_i of 140 eV (cations) and 50 eV (anions). The injected ions lose their kinetic energies by hundreds of collisions with He atoms within several millimeters from the inlet of the ion drift cell. In these collision processes, stable cluster ions survive during CIDs of other cluster ions. Moreover, these magic numbers indicate that cuboid ions with near regular hexahedron such as $n=5$, 14, 23, 38, 63, and 88 are more stable with respect to CIDs than other cuboid ions like 32 ($3\times3\times7$), 53 ($3\times5\times7$), 68 ($3\times5\times9$), and 83 ($3\times5\times11$). This tendency may be ascribed to stability differences due to surface energy of the cluster ions: For example, the magic number of $n=88$ is more clearly observed than that of $n=83$, probably because the surface area of $5\times5\times7$ ions ($n=88$) is smaller than that of $3\times5\times11$ ions ($n=83$). The CIDs of $\text{Na}_n\text{F}_{n-1}^+$ cluster cations were observed by using an electrospray ionization mass spectrometer.³²⁾ In their study, a prevailing dissociation channel was the one leading to a fragment ion with a magic number. Also in the previous surface-impact experiments of $\text{Na}_n\text{F}_{n-1}^+$ cluster cations, low surface-energy fragments have been observed as a result of surface CIDs.²⁶⁾ Present observation indicates that collisional annealing was efficient in the ion-mobility measurement especially at high injection energy conditions, and that the observed mass distribution reflects the stability of cluster ions.

Application to transition metal oxide clusters—(1) Titanium oxide cluster cations and anions

We systematically started IMS study on the first row transition metal oxide cluster ions. We have already reported the geometrical structures of oxide cations of Zn, Co, and Fe, from the IMS measurements, along with the determination of stable cluster sizes and compositions from the ion injection energy dependences of the mass spectra.^{17–19)} Here we present results of other metal oxide ions in addition to Co and Fe, including cations and anions.

Oxide of titanium is known as titanium dioxide, TiO_2 , which has well been investigated as functional materials such as photocatalyst and dye-sensitized solar cell. The bulk crystal is known to have structures called rutile or anatase, in which six oxygen atoms are coordinated to a titanium atom.³³⁾ On the other hand, in the structures of titanium oxide clusters, which were already investigated mainly by quantum chemical calculations, the oxygen coordination number around a Ti atom is 4.^{34,35)}

Figure 5 shows mass spectra of titanium oxide cluster cations and anions at two different ion injection energies E_i obtained in this study. In the mass spectra obtained at $E_i=50$ eV, both cations and anions have several different compositions with comparable intensities. Observed cluster cations at this injection energy have a composition of $\text{Ti}_n\text{O}_{2n-1}^+$ and those with more oxygen atoms, whereas anions have a form of $\text{Ti}_n\text{O}_{2n}^-$ and those with more oxygen atoms. By contrast, cluster ion distribution in the mass spectrum changes with the injection energy E_i . Typically the number of constituent oxygen atoms decreases with increasing E_i , and thus there remains a few chemical compositions at high injection energies. Finally at $E_i=350$ eV, cations predominantly have a form of $\text{Ti}_n\text{O}_{2n-1}^+$. Also the anion mass spectrum has two series of $\text{Ti}_n\text{O}_{2n}^-$ and $\text{Ti}_n\text{O}_{2n+1}^-$, in which the latter is predominant for $n\leq4$ and the former has higher intensity for $n\geq6$. Therefore, titanium oxide anions have one more composite oxygen atoms in average than the cations. From the cross section measurement, we have also determined the geometrical structures in which each Ti atom is coordinated by four O atoms, which is consistent with the results of previous theoretical investigations.^{34,35)}

Fig. 5. Total ion time-of-flight mass spectra of titanium oxide cluster ions obtained at two ion injection energies (E_i) into the ion-drift cell. (a) and (b): Positive ions, (c) and (d): negative ions. (a) and (c): $E_i=50$ eV, (b) and (d): $E_i=350$ eV.

Application to transition metal oxide clusters—(2) Cluster cations and anions of iron oxides and cobalt oxides

Iron oxide has also become useful materials such as catalyst, magnetic storage media, and in biological applications. The bulk was known to have chemical formulas of FeO , Fe_2O_3 , and Fe_3O_4 . However, oxygen-equivalent cluster ions $(\text{FeO})_n^+$ were commonly observed in addition to oxygen-rich clusters such as $\text{Fe}_n\text{O}_{n+1}^+$ and $\text{Fe}_n\text{O}_{n+2}^+$ in gas-phase cluster experiments.^{36,37)} Positive and negative ion TOF mass spectra of iron oxide clusters are shown in Fig. 6 at an ion-injection energy E_i of 250 eV. In these mass spectra, $(\text{FeO})_n^+$

Fig. 6. Total ion time-of-flight mass spectra of iron oxide cluster ions obtained at ion injection energy $E_i=350$ eV. (a) Positive ions, (b) negative ions.

Fig. 7. Total ion time-of-flight mass spectra of cobalt oxide cluster ions obtained at ion injection energy $E_i=350$ eV. (a) Positive ions, (b) negative ions.

and $\text{Fe}_n\text{O}_{n+1}^+$ were predominant for the cations,¹⁹⁾ whereas $\text{Fe}_n\text{O}_{n+1}^-$ and $\text{Fe}_n\text{O}_{n+2}^-$ ions dominated in the anions.

Cobalt oxides are also widely utilized for various materials such as catalyst and semiconductors. Cobalt oxides in the bulk have the same chemical compositions as the iron oxides: CoO , Co_2O_3 , and Co_3O_4 . Therefore cobalt oxide cluster ions were expected to have similar stable compositions with iron oxide clusters. Figure 7 shows TOF mass spectra of cobalt oxide cluster cations and anions at $E_i=250$ eV obtained in the present study. In this figure, although the predominant cluster ion compositions are found to be similar with those of iron oxide cluster ions, they have slightly smaller number of oxygen atoms: $(\text{CoO})_n^+$ and $\text{Co}_n\text{O}_{n-1}^+$ were strongly observed in positive cluster ions, and $(\text{CoO})_n^-$ and $\text{Co}_n\text{O}_{n-1}^-$ were observed in negative cluster ions.¹⁸⁾

From the ion mobility measurements, we have determined iron oxide cluster cations $(\text{FeO})_n^+$ and $\text{Fe}_n\text{O}_{n+1}^+$ ($n=2-9$)¹⁹⁾ and cobalt oxide cluster cations $(\text{CoO})_n^+$ ($n=2-7$) and $\text{Co}_n\text{O}_{n-1}^+$ ($n=5-7$).¹⁸⁾ Both of these cluster ions have ionic bonding nature in which each metal cation binds exclusively with oxygen anions. In addition, transitions from two-dimensional (2D) to three dimensional (3D) structures were observed between $n=5$ and 6 commonly for $(\text{FeO})_n^+$ and $(\text{CoO})_n^+$ cluster ions: 2D ring or sheet structures are most stable for $n \leq 5$, whereas 3D structure such as cubic, tower, or cage become most stable for $n \geq 6$. From a viewpoint of these resemblances between iron and cobalt oxide clusters, it is a little striking result that the stable chemical compositions are different in the present mass spectra. In these metal oxide cluster ions, constituent atoms have electrostatic attractive interactions as mentioned above. Thus the stable compositions in these cluster ions are probably determined mainly by the extent on how the metal atom can donate the electrons. Therefore, the above difference between the clusters of iron oxide and of cobalt oxide probably comes from the slight difference in electronegativity between the iron and the cobalt atoms. This consideration also supports the results of the composition difference between the positive and negative ions for these systems: In most of the metal oxide cluster ions, we have found that the number of composite oxygen atoms in anions are in average one or more higher than that in cations.¹⁹⁾ More systematic discussion may become possible when the same experiments are completed for the rest of the first row transition metal oxides.

CONCLUSION

Ion mobility spectrometry is now taken an interest due to its ability to obtain structural or charge information of the ions. However the drift tube method in this spectrometry can also be used for the investigation of collision-induced-dissociation reactions and other gas-phase collisional reaction kinetics. In the present study we have proven that this technique is also suitable to obtain mass distribution of stable sizes or chemical compositions, especially for ionic bonding cluster ions like alkali halides and metal oxides. For the sodium fluoride cluster ions, we obtained mass spectra in which the cuboid magic number cluster ions were observed intensely. In addition, we have found that the cuboid ions with near regular hexahedron were more predominant than other cuboid ions. As for the metal oxide clusters, we believe that this is the first report on the definite

stable compositions. In titanium oxide clusters, the form of $\text{Ti}_n\text{O}_{2n-1}^+$ series was exclusively observed at high ion-injection energy for cations, whereas $\text{Ti}_n\text{O}_{2n}^-$ and $\text{Ti}_n\text{O}_{2n+1}^-$ were predominant for anions. In oxide clusters of iron and cobalt, different stable compositions were observed, whereas these two metal oxides have almost common composition in the bulk: In iron oxides, $(\text{FeO})_n^+$ and $\text{Fe}_n\text{O}_{n+1}^+$ were predominant for positive ions, and $\text{Fe}_n\text{O}_{n+1}^-$ and $\text{Fe}_n\text{O}_{n+2}^-$ ions dominated in negative ions. In cobalt oxides, $(\text{CoO})_n^+$ and $\text{Co}_n\text{O}_{n-1}^+$ were strongly observed in positive ions, and $(\text{CoO})_n^-$ and $\text{Co}_n\text{O}_{n+1}^-$ were observed in negative ions. Systematic investigations for other transition metal oxide cluster cations and anions, such as vanadium, chromium, and nickel, are now under study in our laboratory.³⁸⁾ Also the detailed structure will be unveiled in the future publications for each metal oxide systems.

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